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For and on behalf of RWS Group Ltd

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Condensation-crosslinking polysiloxane compositions, a process for preparing them and their use

The present invention relates to condensation-crosslinking polysiloxane compositions containing at least one crosslinkable polysiloxane, at least one basic filler, at least one phosphorus compound, at least one alkoxysilane crosslinker, at least one organometallic compound and optionally further fillers, a process for preparing them and their use.

The polysiloxane compositions of the invention, hereinafter referred to as RTV-1 (Room Temperature Vulcanizing 1-component) alkoxy systems, are compositions which are storage-stable in the absence of moisture and cure in the presence of moisture with elimination of alcohols to form elastomers.

Products of this type have been known for a long time and have become established on the market for use as sealants. US 3 294 739, US 3 161 614 and US 3 494 951 disclose the preparation of such compositions from OH- or alkoxy-terminated polysiloxanes, optionally unreactive polysiloxane plasticizers, alkoxysilane crosslinkers, catalysts, fillers and optionally further auxiliaries.

The use of fillers enables the materials costs of RTV-1 compositions to be reduced significantly. However, the fillers serve not only to cheapen the compositions but also have a critical influence on the properties of the RTV-1 alkoxy systems. The concentration and the composition of the fillers used is decisive for the rheological properties of the unvulcanized compositions, e.g. consistency and flow behaviour. Furthermore, they are essential for the mechanical properties of the cured vulcanisates, e.g. ultimate tensile strength, elongation at break and modulus of elasticity. For example, chalks are very frequently used as fillers in RTV-1 compositions. Ground and natural chalk is generally used together with pyrogenic silica. The silica is necessary in this combination for compositions which do not flow to be obtained. As alternatives, it is possible to use precipitated chalks. These chalks can likewise be combined with silica and also with natural chalk. However, in

sufficient concentration, they give compositions having a sufficiently solid consistency even without silica. These compositions display a high ultimate tensile strength and elongation at break together with good adhesion and are therefore very well suited to the typical applications for RTV-1 compositions, for example as sealants.

The use of fillers in RTV-1 compositions, particularly when they are used in relatively high concentrations, can lead to a large increase in viscosity. The high viscosity can present difficulties in the preparation of the compositions, but can also adversely affect their processing. In addition, high filler contents increase the modulus of elasticity of the cured sealants and the elongation at break is reduced. The use of precipitated chalks in particular can lead to very high moduli of elasticity, which are undesirable when the RTV-1 alkoxy systems are used as sealants. A further disadvantage which can occur when fillers, for example chalks and in particular precipitated chalks, are used in RTV-1 alkoxy systems is a reduced storage life of the unvulcanized pastes. If RTV-1 products are stored in the absence of moisture and samples are taken from time to time, the crosslinkability can decrease as a function of the storage time. The compositions continue to alter until crosslinking no longer occurs at all on exposure to atmospheric moisture. RTV-1 alkoxy systems generally have shorter storage lives than other RTV-1 compositions, so that their use is restricted for this reason.

Some additives which can be used in various crosslinking systems to improve the rheological properties of highly filled RTV-1 polysiloxane compositions are known. They alter not only the rheology and the ability of fillers to be incorporated but also the mechanical properties of the vulcanisates. In general, they reduce the modulus of elasticity. However, the addition of such auxiliaries can influence further important properties of the products. Thus, for example, a shortening of the storage life of the unvulcanized compositions or a deterioration in the adhesion properties can occur.

As suitable additives, sulphonic acids, in particular dodecylbenzenesulphonic acid and its salts, are known from EP-A-314313 and EP-A-314314. These RTV-1 alkoxy systems containing sulphonic acids display low moduli of elasticity of the vulcanisates, but the storage stability of the unvulcanized products, which is relatively low without the addition of the sulphonic acid, is not improved by addition of dodecylbenzenesulphonic acid.

In DE-A-2007002, etherified or esterified polyglycols are used in filled

condensation-crosslinking polysiloxane compositions. These products are prepared using various silane crosslinkers having at least one nitrogen atom in the molecule, e.g. oximosilane, aminosilane or aminoxysilane crosslinkers. DE-A-2 653 499 describes phosphoric esters in combination with the same crosslinkers. Suitable additives for alkoxy systems which have a low modulus of elasticity and a good storage stability are not known.

It is therefore an object of the invention to develop filled RTV-1 alkoxy systems which have a low modulus of elasticity and a high elongation at break and which display good storage stability in the unvulcanized state. In addition, the cured material should display good adhesion on many substrates.

It has now surprisingly been found that the known disadvantages of highly filled polysiloxane compositions which cure at room temperature on exposure to atmospheric moisture and liberate alcohols on crosslinking can be very substantially alleviated by adding phosphoric esters and/or polyphosphoric esters as additives to the compositions. These additives lastingly improve both the mechanical vulcanisate properties of the RTV-1 alkoxy systems and their storage stability in the unvulcanized state.

The present invention provides condensation-crosslinking polysiloxane compositions containing

a) at least one crosslinkable polysiloxane containing as terminal reactive radical at least one of the following groups:

$$-O-SiR^1{}_2OH,\ -O-SiR^1(OR^2)_2,\ -O-Si(OR^2)_3,$$

where

R^1 denotes optionally substituted C_1-C_8-alkyl, C_6-C_{14}-aryl or C_2-C_8-alkenyl radicals and

R^2 denotes optionally substituted linear or branched C_1-C_8-alkyl or C_2-C_8-alkoxyalkyl radicals,

and

R^1 and R^2 can be the same or different within the molecule,

b) at least one basic filler and optionally further fillers,

c) at least one phosphorus compound from the group of the orthophosphoric esters of the following formula:

$$O{=}P(OR^3)_{3-n}(OH)_n$$

where

n = 1 or 2 and

R^3 = an optionally substituted linear or branched C_1-C_{30}-alkyl, -acyl, C_2-C_{30}-alkenyl or -alkoxyalkyl, C_5-C_{14}-cycloalkyl or aryl radical or a triorganosilyl or diorganoalkoxysilyl radical which can be the same or different within the molecule,

and/or an ester of polyphosphoric acid,

d) at least one alkoxysilane crosslinker of the formula

$$R^1_xSi(OR^2)_{4-x}$$

where

x = 0 or 1, and R^1 and R^2 can be the same or different within the molecule,

e) at least one organometallic compound and

f) optionally further, auxiliary materials, e.g. plasticizers, coupling agents, stabilizers, pigments, fungicides, etc.

Crosslinkable polysiloxanes a) to be used for the purposes of the invention are polydiorganosiloxanes, preferably polydimethylsiloxanes in which some of the methyl groups may be replaced by vinyl, phenyl, C_2-C_8-alkyl or haloalkyl groups. The polydimethylsiloxanes are essentially linear, but can contain small proportions

of organosiloxy units having a crosslinking action. In a preferred embodiment of the present invention, the crosslinkable polysiloxane a) has a viscosity between 0.1 and 1000 Pas, preferably between 10 and 500 Pas. In addition, the crosslinkable polydiorganosiloxane a) can be partially substituted by unreactive radicals, for example trimethylsiloxy radicals.

In a preferred embodiment of the present invention, the reactive radicals of the polysiloxanes are

$$-O-Si(R^1)_2OH \text{ groups where}$$

R^1 = optionally substituted C_1-C_8-alkyl, C_6-C_{14}-aryl or C_2-C_8-alkenyl radical, where R^1 can be the same or different within the molecule.

The basic fillers b) are, for example, precipitated or ground chalk, metal oxides, sulphates, silicates, hydroxides, carbonates and hydrogencarbonates. Further fillers are, for example, reinforcing and nonreinforcing fillers, e.g. pyrogenic or precipitated silica, carbon black or quartz flour. Both the basic fillers and the further reinforcing or nonreinforcing fillers may optionally be surface-modified. Particularly preferred basic fillers b) are precipitated or ground chalks. Component b) can also be a mixture of fillers.

The phosphorus compounds c) used according to the invention are esters of orthophosphoric acid or polyphosphoric acid or mixtures thereof. Esters of orthophosphoric acid have the following formula:

$$O{=}P(OR^3)_{3-n}(OH)_n,$$

where

n = 1 or 2 and

R^3 denotes an optionally substituted linear or branched C_1-C_{30}-alkyl, -acyl, C_2-C_{30}-alkenyl or -alkoxyalkyl, C_5-C_{14}-cycloalkyl or aryl radical or a triorganosilyl or diorganoalkoxysilyl radical, and R^3 can be the same or different within the molecule.

In a preferred embodiment of the present invention, the phosphorus compound c) is

an ester of orthophosphoric acid having at least one optionally substituted linear or branched C_4-C_{30}-alkyl radical R^3.

Examples of phosphoric esters c) which can be used according to the invention are primary and secondary esters of orthophosphoric acid and mixtures thereof, e.g. di(2-ethylhexyl) phosphate, dihexadecyl phosphate, diisononyl phosphate, monoisodecyl phosphate and mono(2-ethylhexyl) phosphate.

Component c) can likewise be an ester of polyphosphoric acid or a mixture of a plurality of polyphosphoric esters. Salts of orthophosphoric and polyphosphoric esters, e.g. alkali metal salts, are likewise suitable.

Silane crosslinkers d) in the polysiloxane compositions of the invention are alkoxysilanes of the formula:

$$R^1_xSi(OR^2)_{4-x},$$

where

x = 0 or 1,

R^1 denotes optionally substituted C_1-C_8-alkyl, C_6-C_{14}-aryl or C_2-C_8-alkenyl radicals and

R^2 denotes optionally substituted C_1-C_8-alkyl, linear or branched C_1-C_8-alkyl or C_2-C_8-alkoxyalkyl radicals, where R^1 and R^2 can be the same or different within the molecule,

or mixtures thereof.

Preferred alkoxysilanes are tetraethoxysilane, tetra-n-propoxysilane, methyltriethoxysilane, methyltrimethoxysilane, methyltri(2-methoxyethoxy)silane, vinyltrimethoxysilane or vinyltriethoxysilane. Preference is given to methyltrimethoxysilane and vinyltrimethoxysilane. Component d) can likewise be a partial hydrolysate of the alkoxysilane crosslinker.

Suitable organometallic compounds e) are all the catalysts which are customary in condensation-crosslinking polysiloxane compositions according to the prior art.

Particular preference is given to organic titanium and tin compounds. In combination with organic tin compounds, preference is given to using crosslinkable polysiloxanes a) bearing the reactive radicals

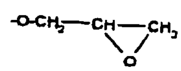
$$-O-SiR^1(OR^2)_2, \qquad -O-Si(OR^2)_3$$

where the radicals R^1 and R^2 are as defined above. Particularly preferred tin compounds are, for example, diorganotin dicarboxylates such as dibutyltin laurate and dioctyltin maleate and also solutions of diorganotin oxides in silicic esters. Preferred titanium compounds are, for example, alkyl titanates such as tetraisopropyl titanate and tetrabutyl titanate and chelated titanium compounds such as diisobutyl bis(ethyl acetoacetate)titanate.

Additives and auxiliary materials f) to be used for the purposes of the invention are preferably plasticizers, coupling agents, pigments and fungicides.

In a preferred embodiment of the present invention, the auxiliary materials f) are silicone plasticizers such as polydimethylsiloxanes having trimethylsiloxy end groups and a viscosity of from 0.1 to 5 Pas, coupling agents such as organofunctional silanes of the formula:

$$X-CH_2-CH_2-CH_2-Si(OR^2)_3$$

where X = $-NH-CH_2-CH_2-NH_2$, 

$$-O-C(O)-C(CH_3)=CH_2,\ -SH,\ -OH,\ -Cl \text{ and}$$

R^2 is as defined above.

The silicone compositions of the invention preferably consist of

100 parts by weight of a),
10 to 250 parts by weight of b),
0.1 to 25 parts by weight of c),
1 to 30 parts by weight of d),
0.1 to 20 parts by weight of e) and
0 to 240 parts by weight of f).

The sum of the auxiliary materials and additives f) preferably has the following composition:

0-100 parts by weight of plasticizer,
0-20 parts by weight of coupling agents,
0-100 parts by weight of pigments,
0-20 parts by weight of fungicides,

the sum total of all the components f) in the mixture being not more than 240 parts by weight.

The present invention also provides a process for preparing the polysiloxane compositions of the invention, in which the components a) to f) are mixed in the absence of moisture.

The phosphorus compounds c) used according to the invention are preferably incorporated into the polysiloxane compositions during the course of the preparation of the compositions. In a particularly preferred embodiment of the present invention, the basic fillers b) and the phosphorus compound c), optionally dissolved in a suitable solvent, are mixed in a preceding operation. Suitable solvents are, for example, water, polar or nonpolar organic solvents, for example alcohols and aromatic or aliphatic hydrocarbons.

The present invention also provides for the use of the polysiloxane compositions of the invention as a sealant, as an adhesive or as a coating.

The following examples serve to illustrate the invention but do not restrict its scope.

Examples

General procedure for the preparation and assessment of the compositions

The preparation of the compositions was carried out in a 1l planetary mixer as described in the following examples. After the preparation was complete, the compositions were introduced into plastic cartridges. Material for the respective further tests was taken from the closed cartridges.

The crosslinking behaviour of the polysiloxane compositions was tested on a glass plate, for which purpose the pastes were applied in a thickness of 2 mm to an area of 40 × 60 mm. After 24 hours, curing of the material right through to the glass surface was tested.

To determine the mechanical properties of the vulcanisates, the pastes were spread in 2 mm thick layers and, after curing at 23°C and 50% relative atmospheric humidity for 14 days, tested in accordance with DIN 53 504. The hardness was determined after 21 days in accordance with DIN 53505.

The storage stability of the products was assessed by storing the pastes in a closed aluminium tube at 50°C. At weekly intervals, samples were taken and tested for crosslinking. If the samples were satisfactorily crosslinked one week after being taken out, the test was passed. Testing of the storage stability at 50°C is a method customary in the assessment of sealants which makes it possible to estimate the storage stability of the products in practice within relatively short periods.

Examples 1 to 4

In a planetary mixer, 44.0 parts by weight of a polydimethylsiloxane having $Si(CH_3)_2OH$ end groups and a viscosity of 50 Pas at 25°C were mixed with 45.0 parts by weight of a precipitated chalk (specific surface area by the BET method = 19 m^2/g) which had been treated with stearic acid with addition of various phosphoric esters to produce a homogeneous paste. The following compounds were used:

Example 1 Di-2-ethylhexyl phosphate

Example 2: Mono-2-ethylhexyl phosphate

Example 3: Monoisodecyl phosphate

Example 4: 1:1 mixture of monoisononyl phosphate and diisononyl phosphate.

8.0 parts by weight of a polydimethylsiloxane having $-OSi(CH_3)_3$ end groups and 2.5 parts by weight of methyltrimethoxysilane were stirred in and the paste was completed by addition of 1.0 part by weight of diisobutyl bis(ethyl acetoacetate)titanate and 0.1 part by weight of N-aminoethyl-3-aminopropyl-trimethoxysilane.

The compositions of Examples 1 to 4 cured satisfactorily right through to the glass plate within 24 hours. The further properties of the compositions may be found in Table 1.

Comparative Example 5

The procedure of Examples 1 to 4 was repeated, but addition of the phosphoric ester was omitted. This composition, too, was cured completely after 24 hours. However, testing of the storage stability and the mechanical properties showed that the product has unsatisfactory properties. The storage stability of only 2 weeks at 50°C and the poor mechanical properties such as high hardness, low elongation and high E modulus greatly restrict the possible uses of such a product because of the technical disadvantages.

Comparative Example 6

The procedure of Example 5 was repeated with addition of 1.5 parts by weight of dodecylbenzenesulphonic acid. The sealant cured completely after 24 hours. The storage stability of the product is indistinguishable from that of Comparative Example 5 without any additive and at only 2 weeks at 50°C is not satisfactory. The mechanical properties of the vulcanisate are good: the vulcanisate has a high elongation at break and a low E modulus (Table 1).

Table 1: Test results for Examples 1 to 6

Ex. No.	Parts by weight of phosphate	Shore hardness A	Elongation at break [%]	E modulus [N/mm^2]	Tensile strength [N/mm^2]	Storage stability[1)] at 50°C [weeks]
1	1.5	28	880	0.49	2.0	4
2	1.0	17	820	0.41	1.7	10
3	1.1	23	780	0.45	1.7	10
4	1.3	23	780	0.46	1.8	10
5[2)]	-	35	640	0.67	2.6	2[3)]
6[2)]	1.5[4)]	24	930	0.44	2.0	2[3)]

1) The products were still in a satisfactory state after the time indicated

2) Comparative example

3) Composition no longer cures after 3 weeks. The product has suffered significant damage.

4) Dodecylbenzenesulphonic acid

Claims

1. Condensation-crosslinking polysiloxane compositions containing

a) at least one crosslinkable polysiloxane containing as terminal reactive radical at least one of the following groups:

$-O-SiR^1{}_2OH$, $-O-SiR^1(OR^2)_2$, $-O-Si(OR^2)_3$,

where

R^1 denotes optionally substituted C_1-C_8-alkyl, C_6-C_{14}-aryl or C_2-C_8-alkenyl radicals and

R^2 denotes optionally substituted linear or branched C_1-C_8-alkyl or C_2-C_8-alkoxyalkyl radicals, and R^1 and R^2 can be the same or different within the molecule,

b) at least one basic filler and optionally further fillers,

c) at least one phosphorus compound from the group of the orthophosphoric esters of the following formula:

$$O{=}P(OR^3)_{3-n}(OH)_n$$

where

n = 1 or 2 and

R^3 = an optionally substituted linear or branched C_1-C_{30}-alkyl, -acyl, C_2-C_{30}-alkenyl or -alkoxyalkyl, C_5-C_{14}-cycloalkyl or aryl radical or a triorganosilyl or diorganoalkoxysilyl radical which can be the same or different within the molecule,

and/or an ester of polyphosphoric acid,

d) at least one alkoxysilane crosslinker of the formula

$$R^1_xSi(OR^2)_{4-x}$$

where

x = 0 or 1,

R^1 and R^2 can be the same or different within the molecule,

e) at least one organometallic compound and

f) optionally further, auxiliary materials.

2. Condensation-crosslinking polysiloxane compositions according to Claim 1, characterized in that the crosslinkable polysiloxane a) has a viscosity between 0.1 and 1000 Pas.

3. Condensation-crosslinking polysiloxane compositions according to either of Claims 1 and 2, characterized in that the basic fillers b) are precipitated or ground chalks.

4. Condensation-crosslinking polysiloxane compositions according to any of Claims 1 to 3, characterized in that the phosphorus compound c) is an ester of orthophosphoric acid with at least one optionally substituted linear or branched C_4-C_{30}-alkyl radical R^3.

5. Condensation-crosslinking polysiloxane compositions according to any of Claims 1 to 4, characterized in that the alkoxysilane crosslinker d) is tetraethoxysilane, tetra-n-propoxysilane, methyltriethoxysilane, methyltrimethoxysilane, methyltri(2-methoxyethoxy)silane, vinyltrimethoxysilane or vinyltriethoxysilane.

6. Condensation-crosslinking polysiloxane compositions according to Claims 1 to 5, characterized in that the organometallic compound e) is an organic titanium or tin compound.

7. Condensation-crosslinking polysiloxane compositions according to Claims 1 to 6, characterized in that the auxiliary materials f) are plasticizers,

catalysts, coupling agents, pigments, fungicides.

8. Condensation-crosslinking polysiloxane compositions according to Claims 1 to 7, characterized in that they consist of

100 parts by weight of a),
10 to 250 parts by weight of b),
0.1 to 25 parts by weight of c),
1 to 30 parts by weight of d),
0.1 to 20 parts by weight of e) and
0 to 240 parts by weight of f).

9. Condensation-crosslinking polysiloxane compositions according to Claims 1 to 7, characterized in that the auxiliary material f) has the following composition:

0-100 parts by weight of plasticizer,
0-20 parts by weight of coupling agents,
0-100 parts by weight of pigments,
0-20 parts by weight of fungicides,

the sum total of all the components f) in the mixture being not more than 240 parts by weight.

10. Process for preparing the condensation-crosslinking polysiloxane compositions according to Claims 1 to 9, characterized in that the basic fillers b) and the phosphorus compound c), optionally dissolved in a solvent, are mixed in a preceding operation.

11. Use of the condensation-crosslinking polysiloxane compositions according to Claims 1 to 9 as a sealant, as an adhesive or as a coating.

Condensation-crosslinking polysiloxane compositions, a process for preparing them and their use

Abstract

The present invention relates to condensation-crosslinking polysiloxane compositions containing at least one crosslinkable polysiloxane, at least one basic filler, at least one phosphorus compound, at least one alkoxysilane crosslinker, at least one organometallic compound and optionally further fillers, a process for preparing them and their use.